PROPERTIES OF ASPHALT FRACTIONS OBTAINED BY SUPERCRITICAL EXTRACTION WITH PENTANE AND CYCLOHEXANE

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INTRODUCTION

Supercritical fractionation is particularly attractive for asphalt fractionation as it already is used commercially for this purpose. The system explored in this work, like commercial processing, does not provide the separating efficiency of supercritical chromatography, but it provides large fractions for further study.

In earlier work (1) three asphalts were fractionated with a combination of supercritical and room temperature separations. The first step was with supercritical pentane and split the asphalts into top (approximately 60%) and bottom (approximately 40%) fractions. The top 60% was subsequently separated into four fractions with supercritical pentane. The hard bottom 40% was separated into 4 fractions by precipitation from mixtures of varying ratios of pentane and cyclohexane at room temperature.

In this current work three asphalts and three reduced crude feeds were fractionated. However, all the separation was done supercritically using either cyclohexane or pentane.

SUPERCRITICAL FRACTIONATION

The operation of the Supercritical Unit has been described previously (1) but the conditions used in this study were different and are shown in Table 1. The three asphalts were first fractionated into four fractions using supercritical cyclohexane. These are fractions 8, 9, 10, and C1. Fraction C1 was fractionated with supercritical pentane into fractions 5, 6, 7, and P1. Fraction P1 was then fractionated with pentane into fractions 1-4. The reduced crudes were similarly fractionated with cyclohexane but the top material was only separated into four additional fractions with the lightest containing material that would normally be in vacuum gas oil. In each run (i.e., pass through the supercritical unit), the heaviest fraction was insoluble at the initial conditions, the next two fractions precipitated on increase in temperature while the lightest fraction was completely separated from the solvent by a reduction in pressure.

ASPHALT ANALYSIS

Infrared analysis was described previously (1). Corbett analyses were done using a modification of ASTM D4124 (2). Asphalts were aged in pressure oxygen vessels that were described by Lau et al. (3). The asphalt is deposited on aluminum trays in an approximately 1mm film to minimize diffusion effects. The vessels were operated at 300

psi (20.1 bar) oxygen pressure at 160°F (71.1°C), 180°F (82.2°C), and 200°F (93.3°C) for periods of time ranging from 2-28 days depending on the temperature.

Low shear rate limiting dynamic viscosities were measured on a Carri-Med 500 (CSL) Controlled Stress Rheometer using the oscillatory mode. The reported values represent the frequency/shear rate independent viscosities. For samples with viscosities greater than 500,000 poise at 60°C, the dynamic properties were measured at 95°C and shifted using time/temperature superposition as described by Ferry (4) to 60°C.

RESULTS

The fraction distributions are shown in Table I. For the three asphalts used, fraction C1, the top cyclohexane fraction, contains from 60 to 80% of the feed material. The percentages of fractions C1 plus 8 through 10 should add to 100, but do not because of difficulty making accurate material balances. For the reduced crudes, the C1 fraction percentages reported in Table I are probably too high because of possible incomplete cyclohexane removal. The top fractions for the asphalt are remarkably uniform in size, while for the reduced crudes they show the relatively large amount of vacuum gas oil in these feeds. The presence of this large amount of vacuum gas oil in the supercritical phase had a marked effect on the temperatures necessary to precipitate the remaining material as shown in Table I.

The Corbett analyses for the Coastal fractions are shown in Figure 1 and are combined with the fraction sizes from Table I to produce the distribution of the whole asphalt Corbett fractions among the supercritical fractions (Figure 2). Thus 37% of all saturates in the Coastal asphalt is in fraction 1, and 40% of the total asphaltenes is in fraction 9. In general the saturates concentrate in the light fractions and the asphaltenes in the heavy fractions. The aromatics are widely distributed with the naphthene aromatic concentration reaching a maximum in fraction 2 or 3, and the polar aromatic at about fraction 6, although with Texaco (not shown) fraction 8 is the highest and 6 is actually lower than 4, 5, or 7. Stegeman et al. (1, 5) has shown that the molecular size of the material increases markedly with fraction number for the supercritical fractions and the individual Corbett fractions.

There is an obvious discontinuity between fraction 7 (the heaviest pentane fraction) and 8 (the lightest cyclohexane fraction). The excess saturates in fraction 8 and asphaltenes in fraction 7 indicate a lower selectivity with cyclohexane. Fraction 7 is much harder than fraction 8 and fraction 6 is generally significantly harder than fraction 8 but not as hard as 7.

This discontinuity is also demonstrated in Figure 3. In this figure the fractions are ranked with respect to solubility by calculating a number (termed the fraction mean) for each fraction which represents the percent of the whole asphalt which is less soluble than the fraction. For example, a fraction representing the most soluble 10% would be plotted at 95%. The whole asphalts, covering the entire range from 0 to 100% are all plotted at 50%. This figure includes all asphalt fractions having viscosities equal or less that 10^5 poise at 60°C including the whole asphalts. A smooth set of data results except

for the only three cyclohexane fractions (all fractions 8) which are widely separated from the pentane fractions and form their own curve.

Fraction Aging: Figure 4 shows aging of the fractions in terms of carbonyl formation. Carbonyl area is defined on an arbitrary scale in terms of the infrared peak between wavenumbers of 1650 to $1820cm^{-1}$ (3, 6). These data for Fina asphalt aged at $93.3^{\circ}C$ ($200^{\circ}F$) show a phenomenon common to all the asphalts. There is an initial rapid increase in carbonyl area, for all but the lightest material, which increases sharply with fraction number. After this initial rapid rate, the rate decreases and becomes constant indefinitely. At $93.3^{\circ}C$ this constant rate is almost the same for all fractions, although for the Coastal asphalt (not shown) the rate seemed to increase slightly with fraction number. In Figure 5 the same phenomenon is seen for Texaco. The initial jump is smaller than for Fina and there is more effect of fraction number, but again the rate appears to remain unchanged after a short initial period of rapid oxidation.

In Figure 6, the aging of Texaco asphalt and fractions 1 at $82.2^{\circ}C$ is shown in terms of viscosity changes. After an initial rapid change as was seen on the carbonyl plots, the log of viscosity changes linearly with time for all fractions and the whole asphalts. This occurs for all fractions at all temperatures.

One of the most interesting and useful relations between chemical changes and changes in physical properties is the universal linear variation of asphalt log viscosity with growth in the carbonyl area (3, 7, 8). Figures 7 to 9 show that this applies to the asphalt fractions as well. All the aging data at all three temperatures are shown on these graphs. These viscosities are measured at $60^{\circ}C$, but a linear relation exists for viscosities measured at other temperatures as well (3). It has been found that the original unaged material may deviate from these lines.

The anomalous behavior of cyclohexane-separated fraction 8 is shown in Figure 9 where fraction 8 is seen to have lower viscosities as it ages than fraction 6. In general, one observes an increase in the sensitivity of the viscosity to carbonyl growth (hardening susceptibility) with increasing fraction number. The Coastal whole asphalt and fraction 8 appear particularly sensitive to carbonyl formation. This does not in itself assure rapid hardening as this also depends on the rate of carbonyl formation which is strongly affected by temperature.

LITERATURE CITED

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TABLE Ia
Supercritical Fractionation Data: Asphalt Fractions

Fraction	Solvent	T(°C)	P(bar)	Fraction Percentages		
				Coastal	Fina	Texaco
1	n-pentane	149	10.1	16	15	14
2	n-pentane	229	47.0	13	10	11
3	n-pentane	227	47.0	9	9	8
4	n-pentane	224	47.0	3	9	3
5	n-pentane	221	47.0	10	13	11
6	n-pentane	213	47.0	3	5	4
7	n-pentane	204	47.0	12	19	14
8	cyclohexane	307	47.0	19	17	17
9	cyclohexane	299	47.0	9	3	17
10	cyclohexane	288	47.0	6	2	3
P1	n-pentane	149	10.1	42	45	33
C1	cyclohexane	204	10.1	67	80	58

TABLE Ib
Supercritical Fractionation Data: Reduced Crude Fractions

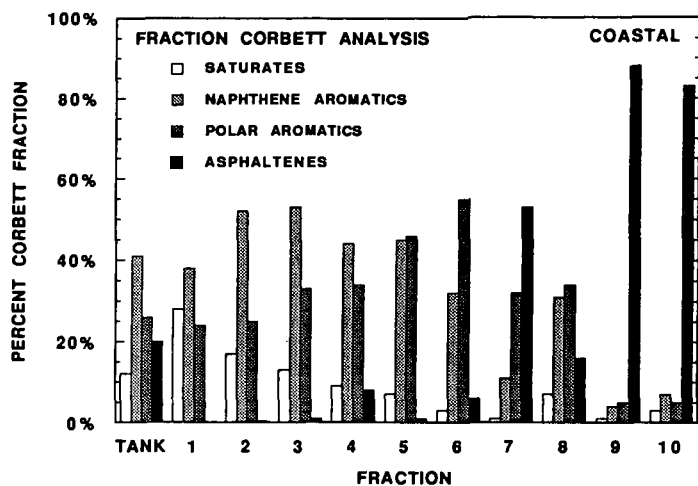| Fraction	Solvent	T(°C)	P(bar)	Fraction Percentages		
				Coastal	Fina	Texaco
1	n-pentane	149	10.1	57	46	44
2	n-pentane	249	47.0	22	43	24
3	n-pentane	232	47.0	4	8	8
4	n-pentane	204	47.0	4	3	6
5	cyclohexane	324	47.0	11	13	13
6	cyclohexane	310	47.0	4	3	7
7	cyclohexane	299	47.0	2	1	3
C1	cyclohexane	204	10.1	88	89	79

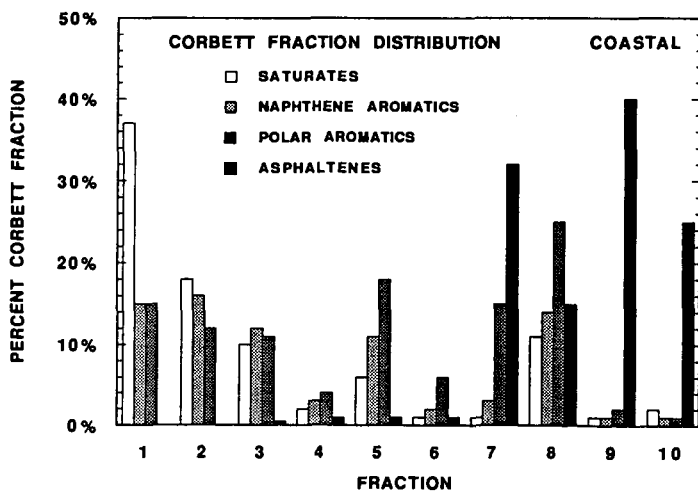Figure 1: Corbett Analysis of the
Supercritical Fractions of the Coastal Asphalt

Figure 2: Distribution of the Whole Asphalt's Corbett Fractions
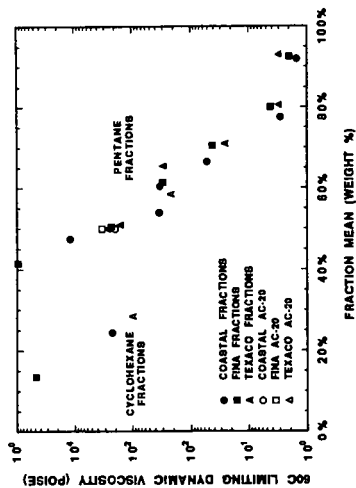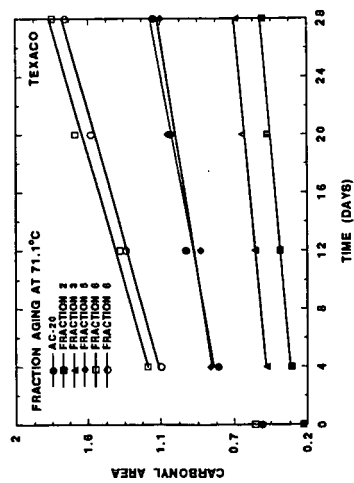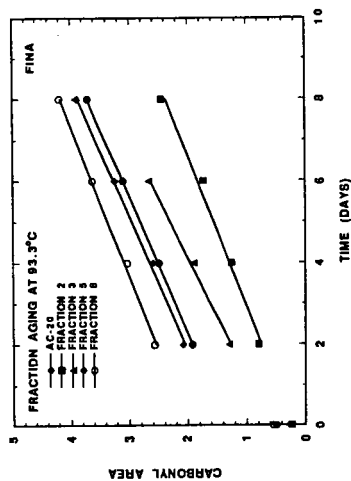Among the Supercritical Fractions of the Coastal Asphalt

Figure 4: Carbonyl Growth with Time of the
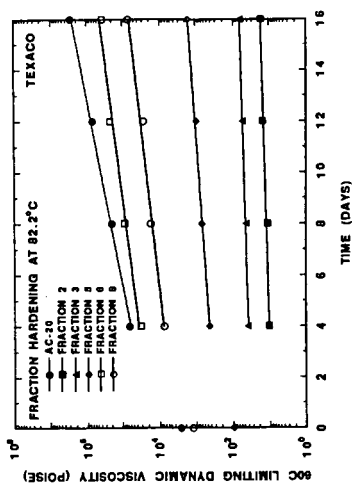Fina Asphalt and Its Fractions Due to Aging at 93.3°C

Figure 6: Hardening with Time of the Texaco Asphalt
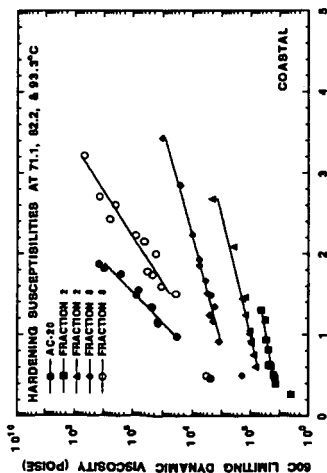and Its Fractions Due to Aging at 82.1°C

Figure 3: Viscosities of the Whole Asphalts
and Their Supercritical Fractions

Figure 5: Carbonyl Growth with Time of the Texaco
Asphalt and Its Fractions Due to Aging at 71.1°C

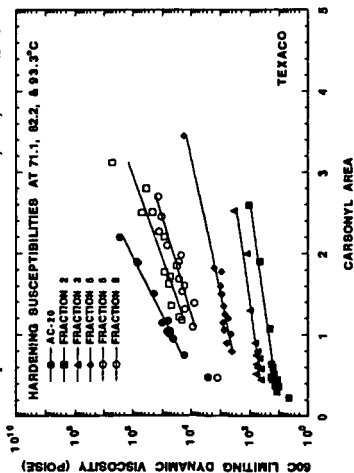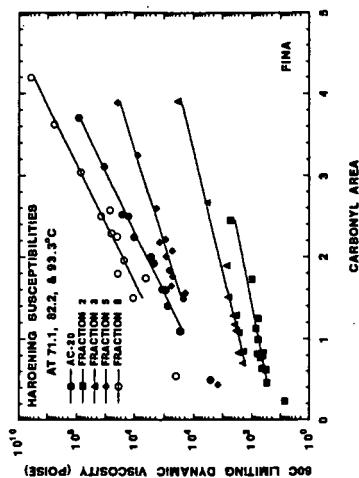Figure 8: Hardening Susceptibilities of the Fina Asphalt and Its Fractions at 71.1, 82.1, and 93.3°C

Figure 7: Hardening Susceptibilities of the Coastal Asphalt and Its Fractions at 71.1, 82.1, and 93.3°C

Figure 9: Hardening Susceptibilities of the Texaco Asphalt and Its Fractions at 71.1, 82.1, and 93.3°C